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# Theoretical study of the ground states of the rare-gas hydrides, HeH, NeH, and ArH

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Harry Partridge, David W. Schwenke, and Charles W. Bauschlicher, Jr.
*NASA Ames Research Center, Moffett Field, California 94035-1000*

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Potential energy curves for HeH, NeH, and ArH are determined using large basis sets and high levels of theory. The computed potential energy curves are in excellent agreement with the experimentally determined model potentials for HeH and NeH, but differ with the model potentials deduced for ArH by Tang and Toennies. We derive a potential based on the *ab initio* calculations and our best estimate of the well depth; using this potential we are able to reproduce the results of the orbiting resonance experiments of Toennies and co-workers.

## I. INTRODUCTION

The ground state potential energy curves of the rare-gas hydrides are essentially repulsive, having only a weak van der Waals minimum. Low levels of theory yield a reasonable description of the repulsive portion of these potentials. However, much better potentials, including an accurate well depth, are required for determining the transport properties of hydrogen atoms in rare-gas mixtures. Also, the rare-gas hydrides are frequently employed in the development of combining relations,[1] because the potential curves for rare-gas dimers and hydrogen molecule are well characterized. Therefore highly accurate rare-gas hydride potentials can be used to check the functional form of the interaction potential used in the combining relations.

In a recent study Tang and Toennies[2] derived model potentials for the rare-gas hydrides, using combining relations, that are in excellent agreement with the best experimentally derived potentials. For example, essentially the same ArH potential is derived using the combining relations and by optimizing the parameters in the model potential to reproduce the orbiting resonance experiment.[3] These rare-gas hydride potentials derived by Tang and Toennies gave rise to nearly identical reduced potentials, providing considerable confidence that the resulting potentials were accurate. Disconcertingly, however, as part of a study[4] on $Ar+H_2$, we found that the *ab initio* $D_e$ value for ArH was only about two-thirds that of the Tang–Toennies model potential. On the basis of other weakly bound systems, the computed potential was expected to be accurate to within ~20%. In addition, we recently found[5] that while our $NaHe^+$ and $NaNe^+$ potentials were consistent with Tang–Toennies model potentials of Ahlrichs *et al.*,[6] our result for $NaAr^+$ was very different. While the bonding in the rare-gas $Na^+$ systems is different than in rare-gas hydrides, the difference between the *ab initio* and model potentials only for the Ar systems was perplexing. Hence, in this work we investigate the computational requirements to determine the interaction potential for the rare-gas hydride systems with an emphasis on ArH. By using very large basis sets and high levels of correlation treatment we are able to overcome the known difficulties in directly computing weakly bound systems and, hence, demonstrate that the potential well for ArH is shallower and broader than that deduced by Tang and Toennies.[2]

## II. METHODS

The difficulties in accurately predicting the spectroscopic constants of a van der Waals potential based solely upon *ab initio* calculations is well documented.[7] In fact, nearly all of the accurate van der Waals potentials available are hybrid potentials or model potentials where the parameters have been optimized to reproduce experimental data.[8] The *ab initio* determinations are complicated because the interaction energies are very small in comparison with the total energies and hence particular care is needed in the design of the calculation. The convergence with the one-particle basis set is very slow and thus it is difficult to accurately compute the intermolecular correlation energy. The basis set must be able to describe the dispersion coefficients and at the same time the basis set superposition error (BSSE) must be very small.

Extensive basis sets are employed in this study. The details of the basis sets are given in the Appendix. The smaller basis sets employed are based on atomic natural orbital (ANO) sets[9] and the larger sets are generalized contractions of the core with the valence functions uncontracted. Even the smallest basis sets employed contain sufficient numbers of diffuse functions to yield accurate polarizabilities for all of the rare gas atoms.

For HeH, we employ a multireference singles plus doubles configuration interaction (MRCI) procedure that is expected to be near the full CI result. First a MRCI calculation is performed [in the self-consistent-field (SCF) molecular orbital basis] that includes all single and double excitations away from all distributions of the three electrons among six $a_1$, two $b_1$, and two $b_2$ orbitals. This is followed by the same MRCI treatment using the natural orbitals of the first MRCI calculation. At all $r$ values the reference space comprises more than 99.9% of the final CI wave function. A similar procedure has been employed for $H_3$ (Ref. 10) where it was shown that the MRCI energies differed from the full CI results by $< 1\ \mu E_h$. For HeH, this procedure reproduces the full CI energies of Knowles *et al.*[11] to within $0.02\ \mu E_h$.

For the larger systems electron correlation is included using the SCF based modified coupled pair functional (MCPF) method[12] and coupled cluster single plus double excitation method with a perturbational estimate of triple excitations,[13] denoted CCSD(T). The CCSD(T) method has been shown[14] to accurately describe the correlation contribution when the SCF is a good zeroth-order description, as is the case for the rare-gas hydrides. Additionally, calibration calculations are performed for ArH using complete active space SCF/averaged coupled-pair functional[15] (CASSCF/ACPF) and interacting correlated fragmented (ICF) approaches.[16] Two active spaces are employed. In the first, the Ar $3p$ and $3d$ orbitals and the H $1s$ orbitals are active. While the Ar $3s$ electrons are not included in the CASSCF active space, they are correlated at the CI level. In the second, the Ar $3s$, $4s$, and $4d$ orbitals are added to the active space. Following the notation of Lengsfield *et al.*,[16] the ICF calculations derived from these two active spaces are designated ICF-2 and ICF-3, respectively. A similar notation is used for the ACPF calculations. Because of the size of the resulting CI expansions, reference selection was required; all spin couplings of configurations with coefficients larger than a selected threshold for a range of $r$ values are included as references.

We computed the BSSE using the full counterpoise correction.[17] For the calculation of the BSSE at the CI level we attempted to employ a reference list equivalent to that used for ArH. If the H-like orbital was occupied in the ArH reference configuration, the H orbital occupation was reduced by one in the reference list in the BSSE calculation. When the H orbital was unoccupied in the ArH reference, then a $\sigma$ electron was removed. For the BSSE calculations, the same active space was used as for the molecular system with the H orbital frozen (except for orthogonalization) in its long range form. We also attempted to employ a CAS-fragment approach[18] (where the infinite separation orbitals, after orthogonalization, are used at all $r$ values) to determine the BSSE. However, the CAS-fragment BSSE corrections were unreliable; these BSSE corrections did not monotonically increase with decreasing $r$, for example. At all levels, the Rg(H) BSSE was small in comparison to the interaction energy. The H(Rg) BSSE was insignificant, $<0.02\ \mu E_h$ even at the shortest bond distances considered. All of the computed results were corrected for the BSSE unless otherwise noted.

The SCF/MCPF and MRCI/ACPF calculations were performed using the SEWARD (Ref. 19)–SWEDEN (Ref. 20) program system. The closed shell CCSD(T) calculations were performed using TITAN.[21] The open shell CCSD(T) calculations were performed using the program developed by Scuseria.[22] All calculation were performed on the NASA Ames Central Computer Facility CRAY Y-MP or Computational Chemistry Branch IBM RISC System/6000 computers.

## III. RESULTS AND DISCUSSION

TABLE I. Spectroscopic constants[a] for HeH, NeH, and ArH.

| $r_e$ (Å) | $D_e$ (meV) | |
|---|---|---|
| HeH | | |
| 3.53 | 0.616 | Present MRCI |
| | 0.626±0.005 | Present estimate |
| 3.46 | 0.666 | Combining rules[b] |
| 3.59 | 0.601 | Molecular beam and diffusion[c] |
| 3.53 | 0.618 | HFD-B model of Scoles[c] |
| NeH | | |
| 3.46 | 1.346 | Present MCPF |
| 3.44 | 1.491 | Present CCSD(T) |
| | 1.51±0.02 | Present estimate |
| 3.43 | 1.49 | Combining rules[b] |
| 3.40 | 1.46 | BMD ($\rho$) from integral cross section[d] |
| ArH | | |
| 3.67 | 3.42 | MCPF-*g* basis |
| 3.63 | 3.84 | CCSD(T)-*g* basis |
| 3.65 | 3.52 | MCPF-*h* basis |
| | 4.05±0.15 | Present estimate |
| 3.54 | 4.67 | Combining rules[b] |
| 3.55 | 4.64 | Orbiting resonance[b] |
| 3.63 | 3.81 | HFD model[e] |
| 3.62 | 4.16 | Differential cross section[f] |

[a] The spectroscopic constants are computed with a quadratic fit in $1/r$. Computed results are corrected for BSSE.
[b] Reference 2.
[c] Reference 28.
[d] Reference 30.
[e] Reference 34.
[f] Reference 31.

The computed spectroscopic constants are reported in Table I. There are few accurate *ab initio* calculations with which to compare. HeH possibly has the smallest potential well of any ground state atom–atom interaction. Most of the calculations[23] on the rare gas hydrides have been studies of the bound excited states that were not designed to obtain accurate results for the van der Waals minima. The early calculations on HeH are summarized in Ref. 11 and references therein. The agreement of our results with the MCSCF results of Das *et al.*[24] is outstanding, particularly considering these calculations were performed 15 years ago. The agreement is, in part, due to a cancellation of errors. In addition to not correcting for BSSE, the MCSCF procedure employed is now known to slightly overestimate the bonding contributions in the well region. The most accurate previous result for HeH is from the full CI calculations of Knowles, Murrel, and Braga;[11] our computed potential is considerably deeper than their value of 0.498 meV. As our MRCI procedure is essentially a full CI and both potentials have been corrected for BSSE, the difference in the results is due to the much larger basis set employed in this work.

Full CI studies[25] on a number of systems have demonstrated that the principal source of error in large MRCI calculations is deficiencies in the one-particle basis set. Contrary to assumptions in the early 1980s, an error of 20% to 25% in the well depth determined by Knowles *et al.*[11] is not unexpected considering the size of the polarization basis employed. Errors of this magnitude are common for weakly bound systems. Improvements in our basis set (and $n$-particle treatment for NeH and ArH) will unquestionably slightly increase the binding energies and decrease the bond lengths. As a rough estimate of the remaining basis set deficiency, we have employed the magnitude of the BSSE in past work with some success.[26] For HeH, this yields an estimate of the true "nonrelativistic Born–Oppenheimer" binding energy of 0.664±0.048 meV, where the error bar is one-half the BSSE at the computed minimum. While not rigorous, this estimate provides some measure of the reliability of our calculation. We must note, however, that applying this procedure to the results of Knowles *et al.*[11] would give an estimate of 0.50±0.005 meV. This estimate is outside that derived from our results. This points to the limitations in using the BSSE to estimate the basis set incompleteness; it cannot account for serious deficiencies in a basis set, in the case of Knowles *et al.*, the limited *d* and *f* basis set and the lack of diffuse functions.

In order to obtain improved error estimates, two additional basis sets were employed to calibrate our HeH calculations. The first consists of fully uncontracting the basis sets for both He and H. This lowered the total energy for HeH at $r=6.75$ by 5.840 meV but did not affect the binding energy to within our convergence criteria (0.0003 meV) for the CI calculations. The BSSE was essentially the same as for the original basis set, demonstrating that the contraction of the tight functions was not the source of the larger BSSE in this work. The second calibration added two uncontracted *h* functions to He (with exponents of 4.098 and 1.6392) and replaced the $(3p2d1f)$ polarization basis set for H with the $(4p3d2f1g)$ polarization functions from the correlation consistent quintuple-zeta set.[27] This H basis is then supplemented with two diffuse $p(0.0984$ and $0.0394)$, a diffuse $d(0.1972)$, and a diffuse $f(0.35)$ function giving a basis set of the form $(11s6p4d3f1g)/[6s6p4d3f1g]$. The basis set yields a HeH binding energy (at $6.75a_0$) that is 0.005 meV larger than that obtained with the original basis set. These results suggest that further basis set improvements will have only a small effect on the well depth. If we assume that further improvements in the basis set will increase the well depth by no more than 0.01 meV, twice the improvement we obtained, we then estimate the binding energy to be 0.626±0.005 meV; this is obtained by adding 0.005 meV (half of 0.01 meV) to our computed results and assigning this as the uncertainty.

Our computed binding energy for HeH is in very good agreement with some of the experimentally derived potentials. Our computed potential for HeH is shown in Fig. 1 and compared with the Scoles potential (reported in Ref. 28) and the Tang–Toennies combining rule potential.[2] The agreement of our results with the Hartree–Fock plus dispersion (HFD-B) potential of Scoles is exceptional and all of the potentials shown agree as to the long range interaction. Our computed $D_e$ and $r_e$ are nearly identical with the HFD-B potential of Scoles and our computed $D_e$ is only slightly deeper than the model potential deduced from the molecular beam and diffusion data[28] (see Table I). The computed $D_e$ is much larger than the Tang–Toennies model determined by Tang and Yang[29] (not reported in Table I) by fitting the low energy molecular-beam data of Toennies, Welz, and Wolf.[3] Our computed well depth is ~10% smaller than the combining rule result of Tang and Toennies, but this is in agreement with their estimated accuracy for this potential.

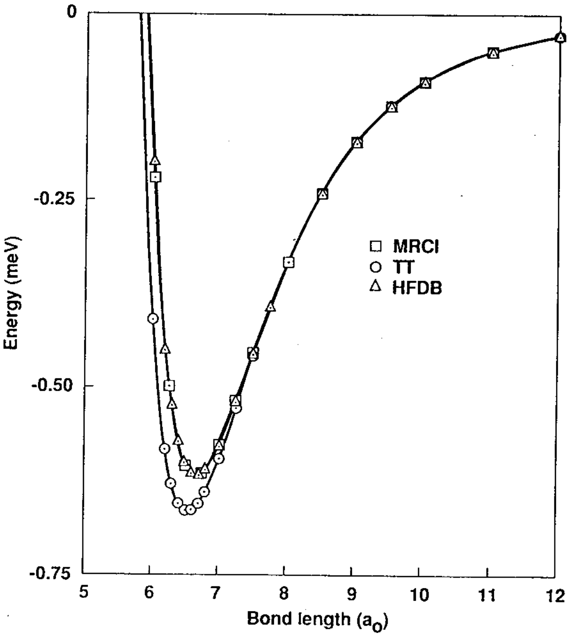

FIG. 1. Comparison of the calculated MRCI potential energy curve for HeH with the Scoles HFD-B potential (Ref. 28) and the Tang and Toennies combining rule potential (Ref. 2).

The MCPF potential energy curve (corrected for BSSE) for NeH is shown in Fig. 2 and is compared with the Tang–Toennies combining rule potential and the Born–Mayer plus dispersion [BMD($\rho$)] potential of Hishi-

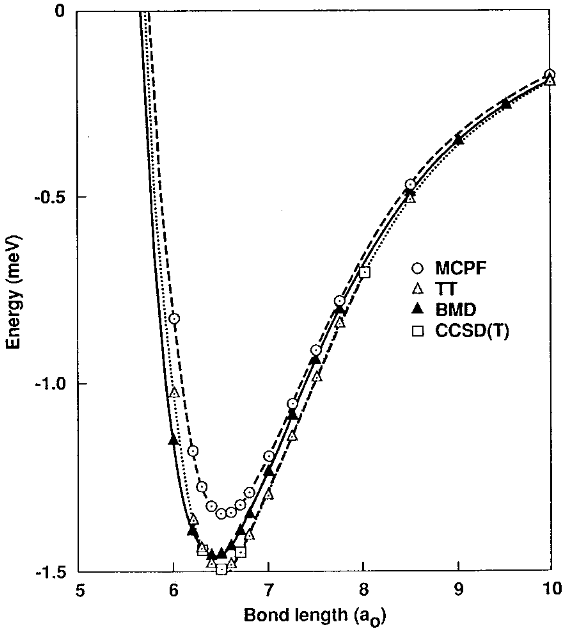

FIG. 2. Comparison of the calculated MCPF potential energy curve for NeH with the Tang and Toennies combining rule potential (Ref. 2) and the BMD($\rho$) potential (Ref. 30). Also shown are the CCSD(T) results—these are the squares superimposed on the Tang and Toennies potential.

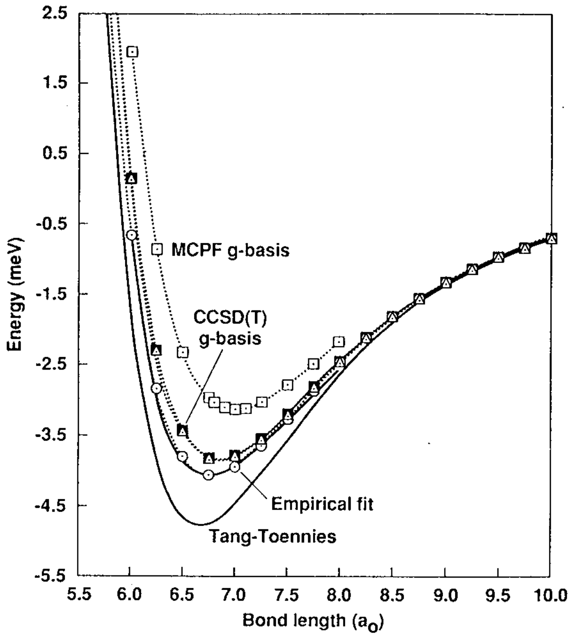

FIG. 3. Comparison of the calculated MCPF potential energy curve for ArH with the Tang and Toennies (Ref. 2) combining rule potential. Also shown shown are the CCSD(T) results and the "empirical" potential derived in this work.

TABLE II. ArH calibration study.[a]

| | $r_e$ (Å) | $D_e$ (meV) |
|---|---|---|
| MCPF results | | |
| Ar basis set tests, with the [6$s$5$p$3$d$2 $f$] H basis | | |
| $h$-basis [12$s$11$p$8$d$8$f$4$g$2$h$] | 3.652 | 3.517 |
| $g$-basis [12$s$11$p$8$d$8$f$4$g$][b] | 3.666 | 3.417(3.460) |
| $f$-basis [12$s$11$p$8$d$8$f$][c] | 3.679(3.708) | 3.192(3.143) |
| $d$-basis [12$s$11$p$8$d$] | 3.800 | 2.419 |
| core basis | 3.703 | 3.363 |
| core basis (2$s$2$p$) | 3.703 | 3.343 |
| Calibration basis | 3.744 | 3.130 |
| Calibration basis results | | |
| MCPF | 3.744 | 3.130 |
| CCSD | 3.75 | 3.004 |
| CCSD(T) | 3.71 | 3.453 |
| ACPF-2(0.01)[d] | 3.72 | 3.289 |
| ICF-2(0.01) | 3.65 | 3.544 |
| ICF-3(0.015) | 3.74 | 2.860 |
| ICF-3(0.01) | 3.73 | 2.986 |

[a] The spectroscopic constants are computed with a quadratic fit in $1/r$. All results are corrected for BSSE.

[b] The effect of expanding the H basis set to [6$s$6$p$4$d$3$f$1$g$] is given in parentheses.

[c] The effect of deleting the $f$ functions on H is given in parentheses.

[d] The reference selection threshold is given in parentheses.

numa.[30] The MCPF $D_e$ is ~10% less than the Tang–Toennies $D_e$ with the BSSE correction being ~10% of the well depth—the BSSE uncorrected MCPF potential (not shown) agrees very well with the Tang–Toennies potential in the well region although it still underestimates the long range interaction slightly. Using the CCSD(T) method (corrected for BSSE) deepens the well and gives results nearly identical with the Tang–Toennies potential. Improvements in the one-particle basis set and correlation treatment will slightly deepen the potential. Using the BSSE correction to estimate the error would give an estimate of 1.54±0.07 meV for $D_e$. As for HeH we suspect that this error estimate is too pessimistic and believe that a more realistic estimate is 1.51±0.02 meV. We note that deleting the most diffuse $s$, $p$, $d$, $f$, and $g$ function on Ne reduces the binding energy by 0.02 meV which is consistent with our estimate.

The ArH MCPF results with the $g$-basis are shown in Fig. 3 along with the Tang–Toennies combining rule potential.[2] The Tang–Toennies potential accurately reproduces the orbital resonance experiments of Toennies *et al.*[3] leading to the suggestion that the resulting potential is very accurate. However, the MCPF and Tang–Toennies potential differ qualitatively. Not only is the *ab initio* potential significantly shallower with a much longer bond length, the calculated potential is noticeably broader. Around the minimum, the calculated energies differ by $<2\ \mu E_h$ over a $0.5a_0$ region. As the MCPF potential does not reproduce the orbital resonance experiments,[3] a major goal of the present study is to calibrate the reliability of the computed potential.

The results of our calibration studies of both the one-particle and $n$-particle basis sets are summarized in Table II. The well depth converges much more slowly with the expansion of the basis set than for HeH or NeH. We obtain a 0.1 meV increase in $D_e$ from $h$ functions suggesting that further expansion of the Ar basis set would increase $D_e$ by on the order of 0.2 meV. The difference in the convergence of the rare-gas-H spectroscopic constants with expansion of the basis set can be predicted based on the convergence of $D_e$ and $r_e$ with the inclusion of higher order dispersion terms in the Tang–Toennies expansion. The slower convergence of this expansion indicates that the higher order terms are more important; the description of the higher order dispersion terms requires the higher angular momentum functions. Expansion of the H basis set also increases the well depth slightly. The $f$-functions on H contribute 0.05 meV. Expansion of the H basis set to the [6$s$6$p$4$d$3$f$1$g$] set increases the binding energy by an additional 0.05 meV. Because the computed $D_e$ differed significantly from the Tang–Toennies result,[2] we also investigated the importance of Ar 2$s$2$p$ correlation. We find that the inclusion of 2$s$2$p$ correlation does not effect the bond length and only slightly reduces the binding energy. Because of the difficulties in accurately computing core correlation effects, we use this result only to estimate the magnitude of the core correlation effects. We conclude that core correlation effects are extremely small and can be ignored. Our basis set calibrations thus suggest that the binding energy at the MCPF basis set limit is 3.67±0.15 meV, where the error bar is half of our estimated basis set error of 0.30 meV.

Improvement of the correlation treatment will also increase the computed binding energy. The CCSD(T) binding energy is ~10% deeper than the MCPF result, as was found for NeH. The deeper well also leads to a shorter bond length as expected. As found in other cases (see Ref.

5 for example), the CCSD approach yields a smaller binding energy than the MCPF; clearly triple excitations are required for accurate results. For both NeH and ArH the MCPF binding energies are consistently 10% smaller than the CCSD(T) results but the resulting potential energy curves are nearly parallel. The CCSD(T) potentials are shifted only slightly to shorter $r$. We estimate that the ArH $D_e$ is $4.05 \pm 0.15$ meV by adding the estimated basis set incompleteness to the CCSD(T) result. Note, using the BSSE to estimate the error leads to a similar result, $3.98 \pm 0.14$ meV.

Because triple excitations account for 13% of the well depth, higher levels of correlation treatment will probably lead to an even larger binding energy. We therefore employed multireference methods to investigate the convergence of the correlation treatment. Unfortunately, the CI expansion lengths quickly became intractable and reference selection was required even for the smallest active spaces. The ACPF-2 binding energy is about halfway between the MCPF and CCSD(T) results. However, we are unable to either tighten the reference selection threshold or expand the active space. Thus the ACPF-2 calculations support the CCSD(T) results over the MCPF, but we are unable to estimate the remaining error at the CCSD(T) level using the ACPF approach.

The ICF approximation leads to smaller CI expansions than the ACPF approach. Using this approach we are able to expand the active space somewhat, but not to convergence. In addition, the ICF results are greatly affected by the reference selection threshold. Thus, the ICF calculations, like the ACPF calculations, cannot be used to calibrate the CCSD(T).

The *ab initio* calculations demonstrate that the ArH potential in the vicinity of the van der Waals minimum is shaped differently than previously thought. However, due to the number of electrons in this system and the slow convergence with basis set, our calculations are not sufficiently converged to definitively determine the potential. However, we can show that there exists a potential based on our estimates of the theoretical potential energy curve that reproduces the scattering data of Toennies *et al.*[3] Consider the empirical potential

$$V(r)=4D_e\left\{\left[\frac{\sigma}{\xi(r)}\right]^{12}-\left[\frac{\sigma}{\xi(r)}\right]^{6}\right\}, \tag{1}$$

with

$$\xi(r)=r-a\{1+\exp[-\alpha(r-r_{1/2})]\}^{-1}. \tag{2}$$

This is a Lennard-Jones potential with a modified argument. The modification is designed to allow the potential to be stretched out in the vicinity of the minimum to mimic the observation that the potential is flatter there. This function contains the five parameters $D_e$, $\sigma$, $\alpha$, $a$, and $r_{1/2}$. We fix $D_e$ and $\sigma$ by requiring that the potential minimum have depth 0.1488 m$E_h$, our estimate of the $D_e$, and that $V(r_0)=0$, where $r_0$ is the experimental value[31] of $5.95a_0$. To confine the "stretching" to the minimum, we take $r_{1/2}=6.8a_0$, our estimate of $r_e$. This leaves the two parameters $\alpha$ and $a$ which were varied by hand to reproduce as best possible the experimental cross sections of Toennies *et al.*[3] The cross sections were computed using phase shifts determined by a banded matrix formulation of the Numerov method.[32] The final parameters are $\alpha=1.2a_0^{-1}$ and $a=0.4a_0$; this potential is also shown in Fig. 3 and is consistent with an extrapolation of the CCSD(T) results. Essentially the same potential is derived by assuming a Tang–Toennies potential form where the repulsive parameters are derived from our estimated $r_e$ and $D_e$ and the experimental value for $r_0$.

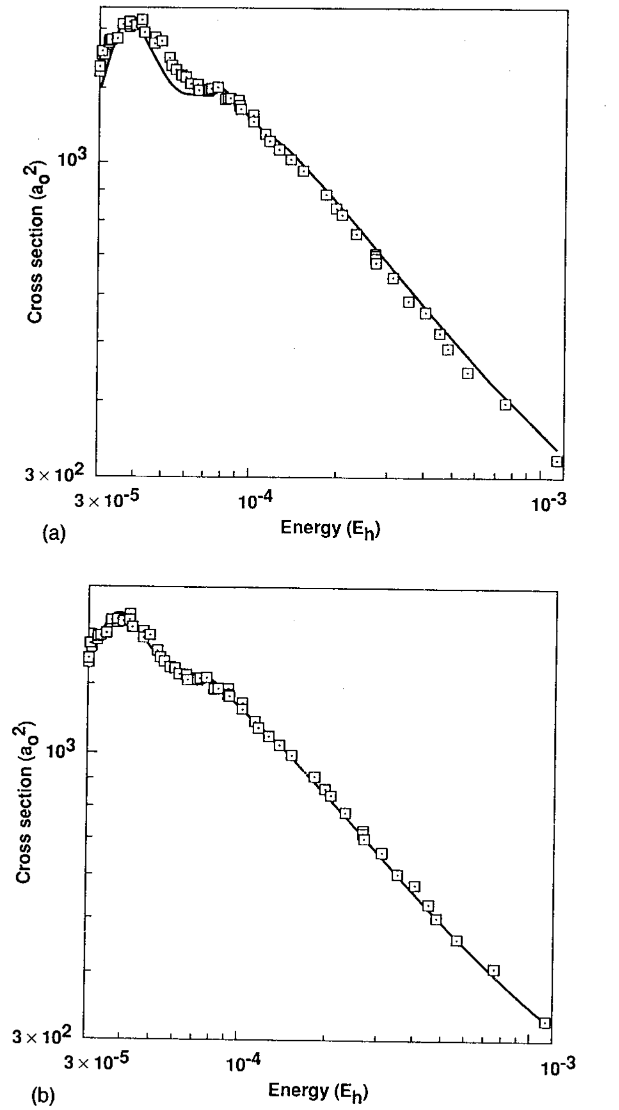

FIG. 4. (a) Cross sections from the Toennies *et al.* (Ref. 3) experiment and the Tang and Toennies combining rule potential (Ref. 2) as a function of translational energy. The scale factor $S=158a_0^2$. (b) Cross sections from the Toennies *et al.* (Ref. 3) experiment and the present empirical potential as a function of translational energy. The scale factor $S=162a_0^2$.

In Fig. 4, we compare the cross sections from the present empirical potential and the Tang and Toennies combining rule potential[2] with the experimental data of Toennies *et al.*[3] The present empirical potential gives cross sections which fit the experimental data with smaller weighted root-mean-square (rms) errors than the Tang and Toennies potential, 1.6 vs 3.7. These rms errors are computed as

$$\text{rms error}=\left(\left(\frac{1}{N}\right)\sum_{i=1}^{N}\{[\sigma^{\text{calc}}(E_i)-S\sigma^{\text{exp}}(E_i)]/[S\Delta\sigma^{\text{exp}}(E_i)]\}^2\right)^{1/2}, \qquad (3)$$

where $N$ is the number of experimental cross sections, $\sigma^{\text{calc}}(E_i)$ is a calculated cross section at energy $E_i$, $\sigma^{\text{exp}}(E_i)$ is an experimental cross section at energy $E_i$, $S$ is a scale factor (the experimental cross sections are reported in arbitrary units), and $\Delta\sigma^{\text{exp}}(E_i)$ is the tabulated error in the experimental cross sections. The scale factor $S$ was determined for each potential by minimizing the rms error. We attempted to further refine the ArH potential by employing the inversion procedure of Heo *et al.*[33] using the experimental cross sections of Toennies *et al.*[3] and both potential curves as initial guesses. However, due to the errors in the experimental data, the inversion procedure did not yield an improved potential. In these calculations no velocity averaging of the theoretical results was performed. Velocity averaging using the parameters of Ref. 3 has only a very small effect on the results.

## IV. CONCLUSIONS

Accurate potential energy curves have been determined for HeH, NeH, and ArH. The computed potential energy curves for HeH and NeH are in agreement with the accepted experimentally derived potentials, with our recommended binding energies being only slightly larger than the experimentally derived values. The errors in the calculations are slightly larger for ArH because of the slower convergence in the computed spectroscopic constants with basis set expansion. The slower convergence is likely to carry over to other Ar systems and suggests that the basis set errors in our NaAr$^+$ results are possibly larger than we had assumed.[5] We note that the effect of electron correlation on $D_e$ is different from ArH; for NaAr$^+$ the CCSD(T) and MCPF binding energies are essentially the same. The computed potential for ArH is both shallower and broader than the ArH potential deduced by Tang and Toennies.[2] However, based upon our extrapolated spectroscopic constants, we can derive a potential energy curve that accurately reproduces the orbiting resonance experiments of Toennies *et al.*[3] While not unique, the existence of such a potential lends credence to our estimate for the ArH binding energy.

## APPENDIX

The hydrogen basis set derived from the 10$s$ hydrogen $^2S$ basis of Ref. 35 supplemented with a diffuse $s$(0.024 86). The innermost 6$s$ functions are contracted based on the SCF orbitals and the outer five functions are uncontracted. This is supplemented with the three $p$, two $d$, and one $f$ function optimized by Dunning[27] and augmented with two diffuse $p$(0.1168 and 0.0467), a diffuse $d$(0.2648), and a diffuse $f$ function (0.5588). All of the polarization functions are uncontracted giving a final basis set of the form $(11s5p3d2f)/[6s5p3d2f]$. This basis set without the diffuse $f$ function was shown[36] to yield an accurate interaction potential for both the repulsive region and van der Waals minimum of $H+H_2$.

The rare gas basis sets are augmented versions of the basis sets we employed in our recent study of the metal ion-rare gas systems.[5] The He $s$ basis set is derived from the $(11s9p)$ set[37] optimized for He($^3P$) supplemented with a diffuse $s$ function (0.0448). An even-tempered ($\beta=2.5$ is used through out this work) $(8p6d4f2g)$ polarization set with $\alpha_0(p)=0.05$, $\alpha_0(d)=0.1518$, $\alpha_0(f)=0.455$, and $\alpha_0(g)=1.366$ is added. The basis set is contracted to $[3s3p2d1f1g]$ using the ANO procedure[9] for the ground state of He atom. The outermost three $s$, three $p$, three $d$, and two $f$ functions are uncontracted and this basis is augmented with one additional diffuse $s$, $p$, and $d$ function, two diffuse $f$ functions, and three diffuse $g$ functions giving a basis set of the form $(13s9p7d6f5g)/[7s7p6d5f4g]$. The atomic polarizability, computed at the CCSD(T) level with a field strength of 0.005 a.u., is $1.386a_0^3$ compared with the $1.333a_0^3$ value estimated by Reinsch and Meyer,[38] and $1.384a_0^3$ value of Rice *et al.*[39]

The Ne basis set is derived from the $(13s8p)$ primitive set of van Duijneveldt.[40] Six even-tempered $d$ and four even-tempered $f$ polarization functions are added, $\alpha_0(d)=0.20$ and $\alpha_0(f)=0.61$, respectively. This basis set is contracted to $[4s3p2d2f]$ using the ANO procedure. The two outermost $s$, $p$, and $d$ and the outermost $f$ primitive functions are uncontracted. This basis is then augmented with three diffuse (even-tempered) $s$ and $p$, two $d$ and $f$ functions, and four $g$ functions $[\alpha_0(g)=0.2039]$ resulting in a final basis set of the form $(16s11p8d6f4g)/[9s8p6d5f4g]$. This basis set yields a polarizability at the CCSD(T) level of $2.676a_0^3$, which is in agreement with the recommended value ($2.67a_0^3$) of Miller and Bederson[41] and the computed value of Rice *et al.*[39]

The Ar basis set is derived from the $(17s12p)$ set[37] augmented with three diffuse even tempered $s$ and $p$ functions (ratio 2.5) and an even-tempered $(8d8f4g2h)$ polarization set ($\alpha_0$=0.0112, 0.016, 0.071, and 0.213 for the $d$, $f$, $g$, and $h$ functions, respectively). This $sp$ primitive set is contracted $[(2+10)s(1+6)p]$ based on the Ar SCF orbitals, where $(n+m)$ indicates that $n$ functions are contracted based on the SCF orbitals and the outermost $m$ primitive are uncontracted. The polarization functions are left uncontracted giving a final basis set of the form $(20s15p8d8f4g2h)/[12s11p8d8f4g2h]$. For calibration a number of other Ar basis sets were employed. The first sets start from the full basis set and delete successively the $h$, $g$, and $f$ basis functions; these basis sets are designated $h$-basis, $g$-basis, etc. by the highest angular momentum functions retained in the basis set. In order to investigate the importance of $2s2p$ correlation, the most diffuse $s$, $p$, $d$, $f$, and $g$ function are deleted and the basis is supplemented with an additional compact $d$ and $f$ function. This basis set is of the form $(19s14p8d8f4g)/[11s10p8d8f4g]$ and is designated core-basis. The final basis sets reported are derived from the $(17s12p6d4f)/[8s7p4d2f]$ set employed in previous work[5] by augmenting the basis with an even-tempered diffuse $s$, $p$, $d$, and $f$ function, giving a basis set of the form $(18s13p7d5f)/[9s8p5d3f]$. This basis set is designated "calibration" and is used to calibrate the $n$-particle treatment. The $f$ functions on hydrogen are deleted when this basis set is used. The calibration basis set and the $h$-basis set yield polarizabilities of 11.30 and $11.14a_0^3$ at the CCSD(T) level. We estimated the $2s2p$ correlation contribution by augmenting the $h$-basis set with a compact $d$ and $f$ and obtain a polarizability of $11.10a_0^3$. These results are in good agreement with the experimental result of 11.07 (Ref. 42) and the value of 11.08 derived from dipole oscillator strength distributions.[43] Our results are also in good agreement with the estimate of Rice *et al.*[44] but suggest that the basis set incompleteness error was larger than their estimate.

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